

PREPARATION VARIABLES FOR THE $GdBa_2Cu_3O_{6.5+\delta}$ SUPERCONDUCTIVE CERAMICS

N. Setter,* C.A. Randall, W. Cao, and A. Bhalla
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

(Received November 16, 1987; Communicated by W.B. White)

ABSTRACT

The thermal conditions for the preparation of $GdBa_2Cu_3O_{6.5+\delta}$ ceramics from mixed oxides and carbonates have been investigated. XRD, SEM, and TEM studies together with resistivity data show a good correlation among the sintering temperature, the lattice parameters and T_c and the resistivity values. The better properties obtained upon sintering at 930° - 940° C fit a correlation between the barium shift, the ordering of the oxygen ions as expected by the rhombicity values and the T_c .

MATERIAL INDEX: Gadolinium - Barium - Copper - Oxide.

Introduction

The properties of the distorted-perovskites high- T_c superconductors are sensitive to the preparation conditions. This has been demonstrated in numerous works and could be responsible for many discrepancies in reported properties. Among the important preparation variables are the sintering temperature and its duration, the sintering atmosphere, the cooling rate, the annealing temperature and the starting raw materials.

Most of the reported works on preparation are concerned with $YBa_2Cu_3O_{6.5+\delta}$ (YBC), but only very few relate systematically the preparation to the properties of the ceramics obtained. Viegers et al. (1) found relationship between the lattice parameters and the properties of quenched YBC samples and their quenching temperature. In $LaBa_2Cu_3O_{6.5+\delta}$ (LBC), Sung-Ik Lee et al. (2) reported that a higher sintering temperature and a higher oxygen vapor-pressure had increased T_{c_a} also for $ErBa_2Cu_3O_{6.5+\delta}$ (EBC) a higher sintering temperature increased T_c (3). However, in the last two examples, as well as in other works, the major objective was the properties measurements and therefore the preparation was only briefly discussed.

*Permanent address: M.O.D., P.O.B. 2250, Haifa 31021, Israel.

Our interest lies in the preparation and processing of superconductive ceramics. In particular the present work is concerned with $\text{GdBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ (GBC) which is of interest as an example for the magnetic-ion containing superconductors. For this material, different works report preparation conditions similar to those of YBC (4-10). The only difference reported so far regards to the oxygen vapor-pressure where it has been found (11) that unlike YBC, oxygen pressure lower than 1 atm. will result in better properties and that the optimum oxygen content was about 0.5 atm.

The parameter that is dealt with in the present work is the sintering temperature of GBC, and the principle question, which could be of interest for other high- T_c superconductive perovskites, is the role of the sintering temperature once the formation of a single phase GBC is achieved.

Preparation

The ceramics were prepared by the mixed-oxides method from CuO 98% (Baker Ltd.), Gd_2O_3 99.99% (RC) and BaCO_3 99.9% (Aesar). The raw materials had been milled in alcohol with zirconia balls and calcined in air at 840°C for 6 hrs. Pressed pellets were sintered in air for 2 hrs, reground, resintered for 4 hrs at different temperatures in the range 870°C - 990°C and then slow cooled at 100°C/hr to room temperature.

Measurements and Results

XRD measurements were performed using a SINTAG PAD V diffractometer. Diffraction patterns from crushed ceramics showed single phase of GBC in all the samples. Lattice parameters were calculated from slow set-up scans ($0.3^\circ/\text{min.}$) at room temperature over 10 diffraction peaks. The results are given in Table I. The rhombicity, that is the difference between a and b parameters, was dependent on the sintering temperature. This is demonstrated

Table I. Lattice parameters of room temperature GBC after sintering at various temperatures

$T_{\text{sintering}} (^\circ\text{C})$	a(Å)	b(Å)	c(Å)	b-a(Å)	$\frac{I_{014/005}}{I_{113}}$	$T_c^*(^\circ\text{K})$
870	3.861 (3)	3.887 (3)	11.659 (7)	0.026	0.33	—
890	3.849 (4)	3.898 (4)	11.688 (4)	0.049	0.30	65
910	3.837 (1)	3.897 (1)	11.697 (2)	0.060	0.45	83
930	3.839 (1)	3.903 (1)	11.707 (2)	0.064	0.52	88
950	3.839 (1)	3.902 (1)	11.709 (2)	0.063	0.67	86
970	3.837 (1)	3.900 (1)	11.703 (2)	0.063	0.61	86
990	3.840 (1)	3.898 (1)	11.692 (3)	0.058	0.58	78

* T_c is taken at the temperature where resistivity had dropped to 50% of its value at the onset temperature.

in Fig. 1 where the splitting of 103 and 013/110 for the different sintering temperatures is presented.

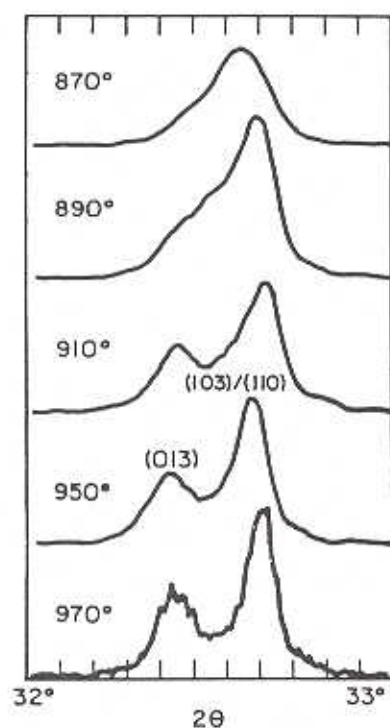


Figure 1. Development of the orthorhombic cell as a function of the sintering temperature, as exhibited by the 103 and 013/110 splitting.

The morphology of the ceramics prepared at different temperatures were studied by SEM (ISI DS 130). After the first sintering, samples treated below 930°C contained minor phases of CuO , BaCuO_2 and $\text{Gd}_2\text{BaCuO}_5$ (green phase) intergrown between the GBC grains, as demonstrated in Fig. 2. Regrinding and second sintering resulted in elimination of the minor phases and

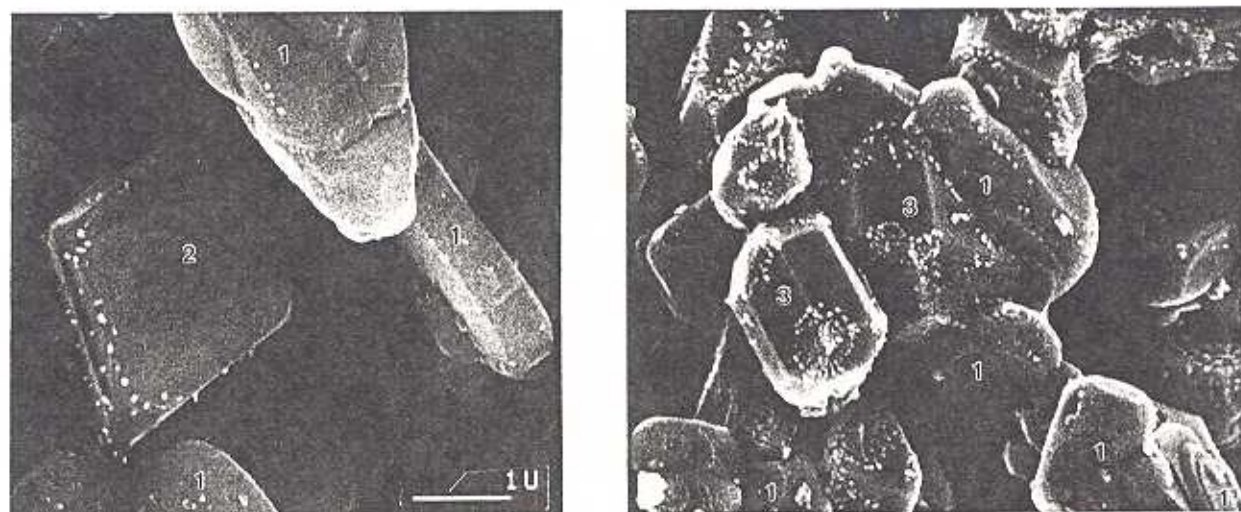


Figure 2. SEM photographs of GBC after first sintering at 910°C showing GBC grains (1), CuO grains (2), BaCuO_2 grains (3).

further growth of the GBC grains (Fig. 3). In all the cases the grains were platy and the grain length increased from $\sim 1 \mu$ for samples prepared at 870°C to $\sim 10 \mu$ for the samples prepared at

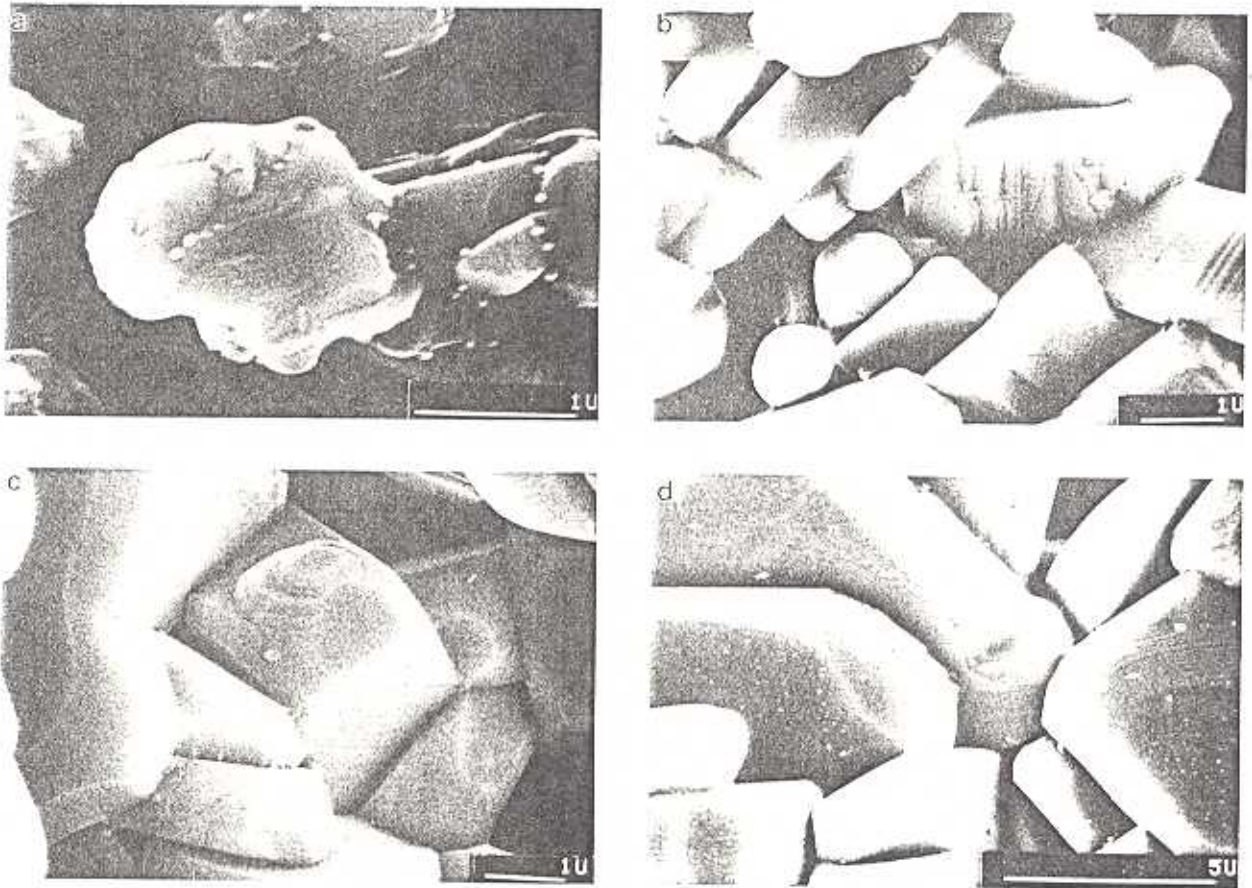


Figure 3. SEM photographs of GBC samples after second sintering at different temperatures a) 870°C , b) 930°C , c) 950°C , d) 970°C .

970°C . In all the cases layer growth was observed.

Further microstructural studies were carried out using TEM. The samples were prepared by both ion beam thinning and crushing. TEM observations were made using a Philips-420 STEM at 120 KV. Microstructural comparisons were made between sintered samples prepared at 870°C and 970°C . The 870°C samples showed a small grain size and these were imbedded in an amorphous material, however the large grained 970°C samples had less amorphous phase. Other microstructural differences existed within the grains. The 870°C samples had a poor representation of ferroelastic domain structure. The domain structure in many grains showed evidence of alteration similar to observations made by Baba-Kishi *et al* (12). However, there was a small percentage of the grains with good ferroelastic domain structure. Selected area electron diffraction of the alteration domain structure revealed spot splitting and dark field imaging of these split spots revealed moire interference patterns within the alteration structure. In the samples prepared at 970°C the majority of grains had good a-b ferroelastic twinned domains. Examples of the differences between the microstructure in the 870°C and 970°C are given in Figures 4 and 5, respectively.

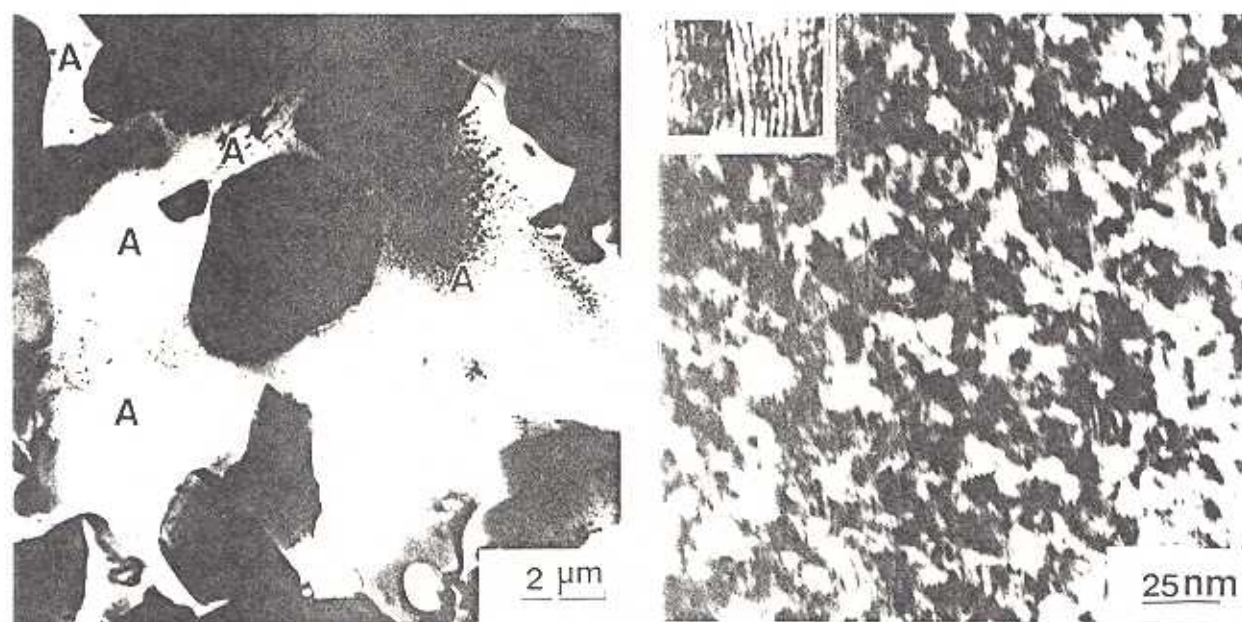


Figure 4a,b. Microstructure of GBC prepared at 870°C (a) grains imbedded in amorphous phase and (b) showing the alteration domain structure. (Insert shows moiré interference pattern within the alteration structure).

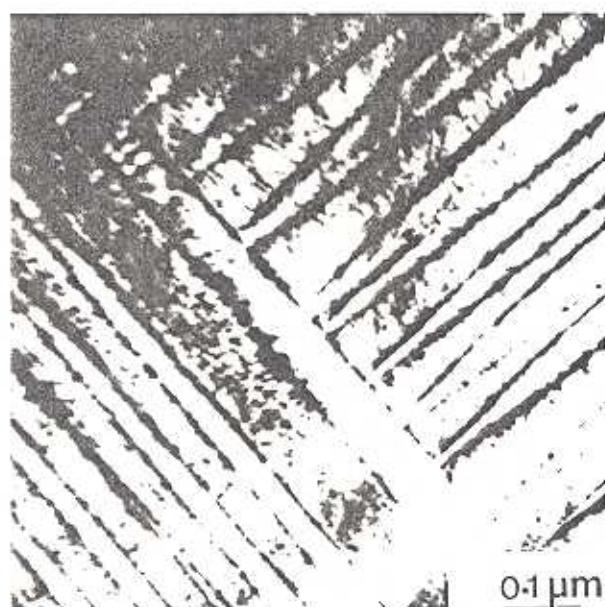


Figure 5. Microstructure of GBC prepared at 970°C showing the a-b ferroelastic domains.

The resistivities of the different samples were measured by the four point technique. The ceramics sintered at 870°C showed semiconductor-type behavior with increasing resistivity upon cooling down to liquid helium temperature. With all other heat treatments, the resistivity dropped to zero (the resolution was $< 10^{-8} \Omega\text{-cm}$). Some of the resistance vs. temperature curves are shown in Fig. 6.

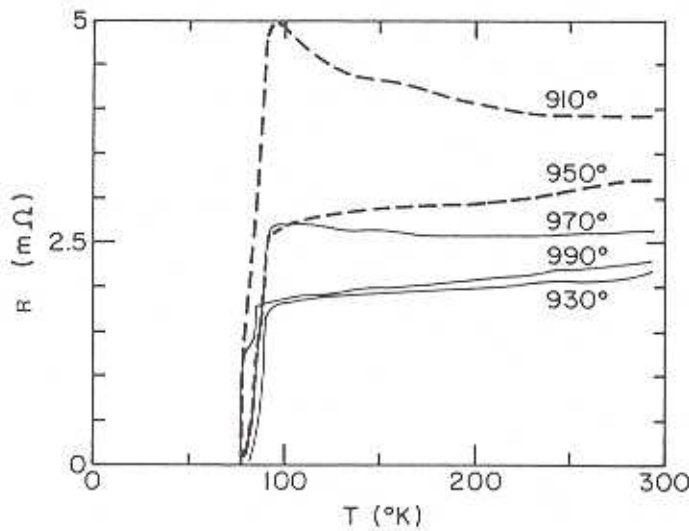


Figure 6. Typical resistance curves for samples sintered at various temperatures.

Discussion

In the present study an attempt has been made to isolate the effect of sintering temperature from other parameters and therefore all the samples have been prepared in the same manner and cooled at the same rate down to room temperature. Oxygen treatment was eliminated in order to avoid complicating factors, as it had been found, in agreement with Hack *et al.* (11), that for GBC, sintering in air resulted in a lower resistivity than sintering in pure oxygen.

The results show that in order to obtain better properties, the GBC compound has to be prepared at a higher temperature than its formation temperature. The XRD data gives a possible explanation to these results. Three major changes occur in the XRD pattern upon increasing the sintering temperature (up to an optimal temperature): 1) the rhombicity increases, 2) the *c* parameter increases and 3) the 014/005 intensity increases.

The 014/005 intensity is related to the shift of the barium ion off the undistorted cubic position. In a hypothetical normal cubic position the barium ion would have 12 oxygen neighbors and the position (0.5, 0.5, 0.1666) where the gadolinium ion is in the (0.5, 0.5, 0.5) site. In the distorted perovskite structure, the barium which has less than the required 12 oxygen neighbors is shifted. In the $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound, which is tetragonal and highly oxygen deficient, the barium ion has eight oxygen neighbors and is shifted to (0.5, 0.5, 0.1934) (13). In the orthorhombic YBC compound the barium has 10 oxygen neighbors and is shifted, though to a lesser extent to (0.5, 0.5, 0.1838) (14). In YBC the order-disorder transition of the oxygen atoms takes place when the oxygen content is still low, 0.3 O^{2-} in the plane of the Cu^{2+*} ions, according to Viegers *et al.* (1), relative to 0.9-1 in the final superconductive state. In YBC prepared in pure oxygen and therefore likely to have more bound oxygen at a given temperature relative to air-prepared sample, the o-t transition takes place at a higher temperature.

It is tempting to argue that only when there is low oxygen content in the Cu^{2+} layer, and therefore the Ba ion is shifted up, only then ordering will initiate. Therefore, material prepared at too low temperature, where the Cu^{2+} layer is at equilibrium with a higher content of oxygen, ordering is difficult because the barium ion is less strongly shifted. In other words, the preparation of a good superconducting oxygen-ordered material could not be completed at low temperatures.

The term Cu^{2+} is given to the copper ions of valency higher than 2.

The above argument is in agreement with our observations: the rhombicity is low when 014/005 intensity is low--which means that the ordering is not fully accomplished, and at the same time the c parameter is low because the neighboring barium ions in the unit cell are screened by the oxygen of the Cu^{+2} layer. Also the TEM observations support the above explanation; at 870°C ordering is not fully achieved and therefore the a and b parameters are different for different regions and a domain alteration structure is created.

Although the above discussion draws an acceptable picture which relates the barium shift and the oxygen content at the preparation temperature to the characteristics of the material at RT, it does not give a physical explanation to the correlation between the higher rhombicity and the high T_c . This correlation exists in our results, as shown in Fig. 7. Still, one has to remember that the low rhombicity was accompanied by a glassy phase, and this phase can also be responsible for the deterioration of the properties, either through its own poor properties or through causing an off-stoichiometric composition of the GBC where slight off-stoichiometry can result in poorer properties. This point remains unclear at present.

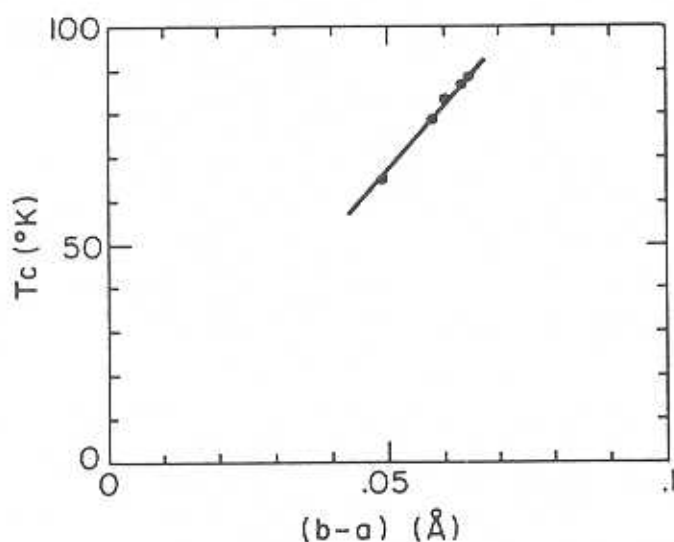


Figure 7. The relation between the rhombicity and T_c .

Acknowledgements

The authors are thankful to Professors L.E. Cross, S.K. Kurtz, R.E. Newnham, and R. Roy for the useful discussions and encouragement during the work. The work has been supported by the ONR-DARPA grant under the contract No. N00014-86-K-0767

References

1. Viegers, M.P.A., deLeeuw, D.M., Mutsaers, C.A.H.A., Smoorenburg, H.C.A., Hengst, J.H.T., deVries, J.W.C., and Zalm, P.C., *Appl. Phys. Lett.*
2. Lee, S.I., Golben, S.P., Lee, S.Y., Chen, X.D., Song, Y., Noh, T.W., McMichael, R.D., Gaines, J.R., Cox, D.L., and Patton, B.R., *Phys. Rev.* **36**, 2417 (1987).
3. Golben, S.P., Lee, S.I., Lee, S.Y., Song, Y., Noh, T.W., Chen, X.D., Gaines, J.R., and Tettenhorst, R.T., *Phys. Rev.* **35**, 8705 (1987).
4. Hulliger, F and Ott, H.R., *Phys. B* **67**, 291 (1987).

5. Mei, Y., Green, S.M., Reynolds, G.G., Wiczynski, T., Luo, H.L., and Politis, C., *Z. Phys. B* 67, 303 (1987).
6. Ho, S.C., Hoy, P.H., Meng, R.L., Chu, C.W., and Huang, C.Y., *Solid State Commun.* 63, 711 (1989).
7. Xiao, G., Streitz, F.H., Gavrin, A., and Chien, C.L., *Solid State Commun.* 63, 817 (1987).
8. Brown, S.E., Thompson, J.D., Willis, J.O., Aikin, R.M., Zirngiebl, E., Smith, S.L., Fisk, Z., and Schwarz, R.B., *Phys. Rev.* 36, 2298 (1987).
9. Yang, K.N., Dalichaouch, Y., Ferreira, J.M., Lee, B.W., Neumeier, J.J., Torikachuilin M.S., Zhou, H., and Maple, M.B., *Solid State Commun.* 63, 515 (1987).
10. Thompson, J.R., Sekula, S.T., Christen, D.K., Sales, B.C., Boatner, L.A., and Kim, Y.C., *Phys. Rev. B* 36, 718 (1987).
11. Hauck, J.H., Bickmann, K., and Zucht, F., *Z. Phys. Rev. B* 67, 295 (1987).
12. Baba-Kishi, K.Z., Barber, D.J., and Whatmore, R.W. (preprint).
13. Steinfink, H. and Swinnea, J.S., *J. Mat. Res.* 2, 424 (1987).
14. Beech, F., Miraglia, S., Sanforo, A., and Roth, R.S., *Phys. Rev.* 35, 8778 (1987).